Class | Adm No 837

Candidate Name: _____

H

millennia institute

2013 Preliminary Examination II
Pre-university 3

H2 CHEMISTRY 9647/03

Paper 3 Free Response **Friday, 20 Sep 2013**

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet
Graph Paper

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.
At the end of the examination, fasten all your work securely together.

Begin each question on a fresh sheet of paper.

Answer any **four** questions.

1. **(a)** State and explain in terms of electronic structure, **two** characteristic chemical properties of transition metals or their compounds.

[4]

(b) Transition element complexes such as those of iron are common reagents in colourful demonstrations of redox reactions. In one particular demonstration, the following observations were made.

When aqueous iron(III) sulfate was added to aqueous sodium iodide, the reaction mixture turned brown. The brown colour is discharged upon addition of aqueous sodium hexacyanoferrate(II), $Na_4Fe(CN)_6$.

On the other hand, when aqueous sodium hexacyanoferrate(III), $Na_3Fe(CN)_6$, was added to a fresh sample of the aqueous sodium iodide, the colour of the reaction mixture remained unchanged.

(i) Explain the above observations using relevant data from the Data Booklet.

(ii) Comment on the relative stability of the different oxidation states of iron in the presence of different ligands.

[5]

(c) Haemoglobin (Hb) is composed of 4 polypeptide chains: two alpha chains and two beta chains of polypeptides. Each chain contains one haem group, each of which contains one iron ion. The iron is the site of oxygen binding; each iron can bind one O_2 molecule thus each haemoglobin molecule is capable of binding a total of four O_2 molecules.

The iron–oxygen interaction is very weak; the two can easily be separated without damaging the haem unit or the oxygen molecule. The binding of an oxygen molecule to the iron in a haem unit is therefore completely reversible.

(i) Explain how O_2 molecule binds to the Fe of the haem group.

1. (c) (ii) Each Hb molecule has a *complex quaternary structure*. Briefly describe what this means.

(iii) A haemoglobin molecule in which the iron has separated from the oxygen molecule is called *deoxyhaemoglobin*. Blood containing red-blood cells filled with O_2 is brighter red. Suggest an explanation for the observation of this colour.

(iv) Haemoglobin is susceptible to denaturation. Explain the term *denaturation* as applied to proteins and state two types of R group interactions that can be disrupted when heat is applied to proteins.

[7]

(d) Iron(II) ethanedioate, FeC_2O_4, reacts with manganate(VII), MnO_4^-, forming Fe^{3+} and carbon dioxide. In an experiment, 0.144g of FeC_2O_4 reacted with 20.0 cm^3 of 0.150 mol dm^{-3} of MnO_4^-.

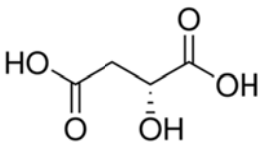
(i) Write an ion-electron equation for the oxidation of FeC_2O_4 to Fe^{3+} and carbon dioxide.

(ii) Determine the oxidation number of manganese in the product formed after the reduction of manganate(VII).

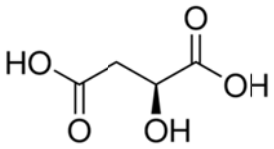
[4]

[Total: 20]

2. **(a)** Malic acid is an organic dicarboxylic acid found in wines, sour apples and some other fruits. Malic acid has two stereoisomeric forms as shown below:



D-Malic acid

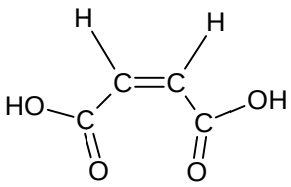


L-Malic acid

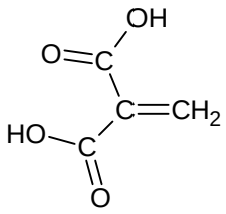
(i) State a characteristic difference between D- and L-Malic acid.

(ii) With the aid of a diagram, explain why malic acid is soluble in water.

(iii) Malic acid can be dehydrated to give compound **K**. Compound **L** is an isomer of compound **K**.



compound **K**

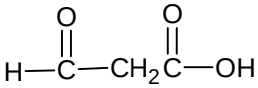


compound **L**

State the type of isomerism exhibited.

(iv) Compound **L** in **(a)(iii)** decolourises acidified potassium manganite(VII). Draw the structure of the organic product.

(v) The structure of 3-oxopropanoic acid is shown below.



3-oxopropanoic acid

Suggest how you can make malic acid from 3-oxopropanoic acid in **two** steps, showing the reagents and conditions necessary as well as the structure of the intermediate.

[8]

2. (b) A student carried out an experiment to investigate the rate of reaction between sodium and malic acid. A freshly cut piece of sodium weighing 0.0690 g was added to a large excess of malic acid.

The volume of gas evolved was measured at room temperature and pressure over a 30-min time interval. The following results were obtained.

Time /min	0	5	10	15	20	25	30
Volume of gas /cm^3	0.0	8.5	15.0	20.5	25.0	27.5	31.0

(i) Write a balanced equation for the reaction between sodium and malic acid.

(ii) Calculate the maximum volume of gas evolved at room temperature and pressure if the reaction goes to completion.

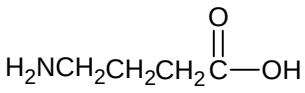
(iii) What do you understand by the term *order of reaction*?

(iv) Using the graphical method, show that the overall kinetics of the reaction is first order.

(v) In this experiment, the kinetics appears to be zero order with respect to malic acid initially. Suggest a reason for this.

[7]

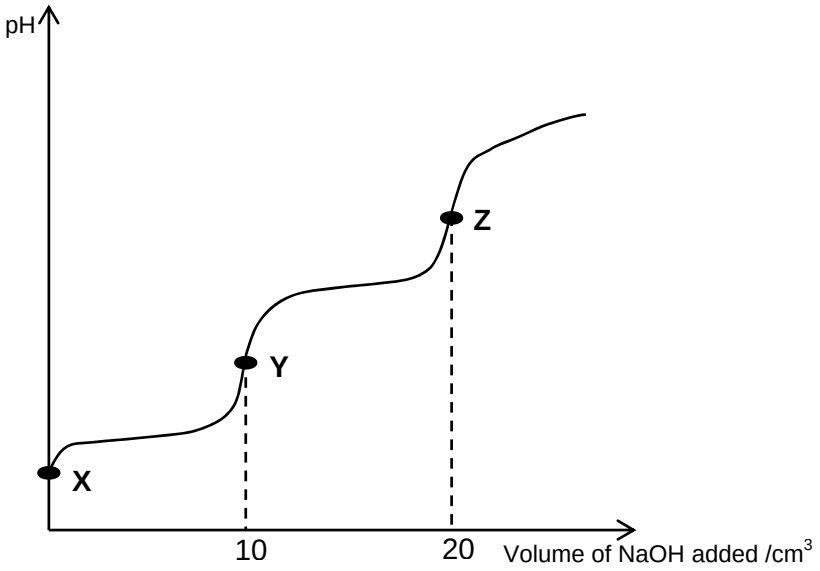
2. **(c)** 4-aminobutanoic acid, also known as GABA, can also be synthesised from 3-oxopropanoic acid in a few steps.



GABA

The two pK_a values associated with 4-aminobutanoic acid are 4.23 and 10.43.

A sample of GABA requires 20 cm^3 of 1.0 mol dm^{-3} NaOH for complete neutralisation. The following diagram is a titration curve, showing how the pH of GABA changes with volume of NaOH added.



(i) Draw the structures of the predominant species of GABA at **X**, **Y** and **Z**.

(ii) State the pH and the volume of NaOH added when **Y** and **Z** are equimolar.

[5]

[Total: 20]

3. **(a)** Calcium is a mineral that is found naturally in foods. Calcium is necessary for many normal functions of the body, especially bone formation and maintenance.

Calcium sulphate, $CaSO_4$, is a salt of calcium. It is used as a coagulant in products like tofu.

(i) Draw the dot-and-cross diagram to show the bonding in sulfate ion. State the shape and the bond angle.

(ii) Using the following data, construct an energy level diagram to calculate the enthalpy change of solution of $CaSO_4$.
Include state symbols in your diagram.

enthalpy change of hydration of calcium ion	– 1562 kJ mol^{-1}
enthalpy change of hydration of sulfate ion	– 1166 kJ mol^{-1}
lattice energy of calcium sulfate	– 2710 kJ mol^{-1}

(iii) Hence predict whether $CaSO_4$ becomes more or less soluble when temperature increases. Explain your answer.

[9]

(b) Calcium sulfate is a component of the grout used in between the tiles in swimming pools. Calcium chloride is added into swimming pools to prevent calcium sulfate in the grout from dissolving.
The solubility product of $CaSO_4$ at 25°C is 2.4×10^{-5} mol^2 dm^{-6}.

(i) Write an expression for the solubility product, K_{sp}, of $CaSO_4$.

(ii) If 5.555 kg of calcium chloride was added to a wading pool containing 3000 dm^3 of water, calculate the maximum concentration of sulfate ions in the water.

(iii) Explain qualitatively how the added calcium chloride helps to prevent calcium sulfate in the grout from dissolving.

[6]

3. **(c)** Calcium iodate(V) is another calcium salt with the formula $Ca(IO_3)_2$.

At high temperatures, Calcium iodate(V) undergoes decomposition to form a white solid, violet vapour and a colourless gas which relights a glowing splint.

(i) Construct a balanced equation, with state symbols, for the decomposition process.

(ii) Describe and explain how the thermal stabilities of the Group II iodate(V) vary down the group.

(iii) Predict the relative thermal stability of calcium chlorate(V) compared to calcium iodate(V). Explain your answer.

[5]

[Total: 20]

4. **(a)** A rechargeable battery contains inert platinum electrodes immersed in solutions containing a mixture of vanadium compounds in different oxidation states. One half cell contains a mixture of $VO_2^+(aq)$ and $VO^{2+}(aq)$ and the other half cell contains $V^{2+}(aq)$ and $V^{3+}(aq)$.

(i) By reference to the Data Booklet, choose two half-equations to construct the full equation for the reaction that occurs during discharge. Calculate the $E°_{cell}$.

(ii) Sketch a fully labelled diagram of the above cell, showing the direction of the electron flow.

(iii) Write the equation for the charging process.

(iv) Predict, with reason, the effect of adding water to the half cell containing $V^{2+}(aq)$ and $V^{3+}(aq)$ on the $E°_{cell}$.

[8]

4. **(b)** Vanadium forms many complexes. The oxidation number of vanadium in a complex was determined as follows:

A 0.0423 mol sample of the complex cation with an inert anion was dissolved in water and the solution was made up to 250 cm^3. A 25.0 cm^3 portion of this solution reacted exactly with 21.15 cm^3 of 0.0800 mol dm^{-3} aqueous acidified potassium manganate(VII) solution. If the oxidation number of vanadium in the product was +5, calculate the original oxidation number of vanadium in the complex.

[4]

(c) *α*-Hydroxy acids (AHAs) such as lactic acid, $CH_3CH(OH)COOH$, are naturally occurring carboxylic acids which are well-known for their use in the cosmetic industry.

When orange potassium dichromate(VI) is added to lactic acid, compound **G** is formed and the solution turns green. Compound **H** is formed when **G** is reacted with hydrogen cyanide in the presence of a trace amount of sodium cyanide at 10 – 20 °C.

(i) Excess 2,4-dinitrophenylhydrazine was added to compound **G**. Write a balanced equation for this reaction.

(ii) State the type of reaction undergone when **G** reacts to form **H**.

(iii) Draw the **displayed** formula of compound **H** formed and explain why **H** has no optical activity.

(iv) Compound **J** is formed when **H** is treated with lithium aluminium hydride. Deduce the structural formula of compound **J**. Hence, suggest a test that distinguishes **J** and lactic acid.

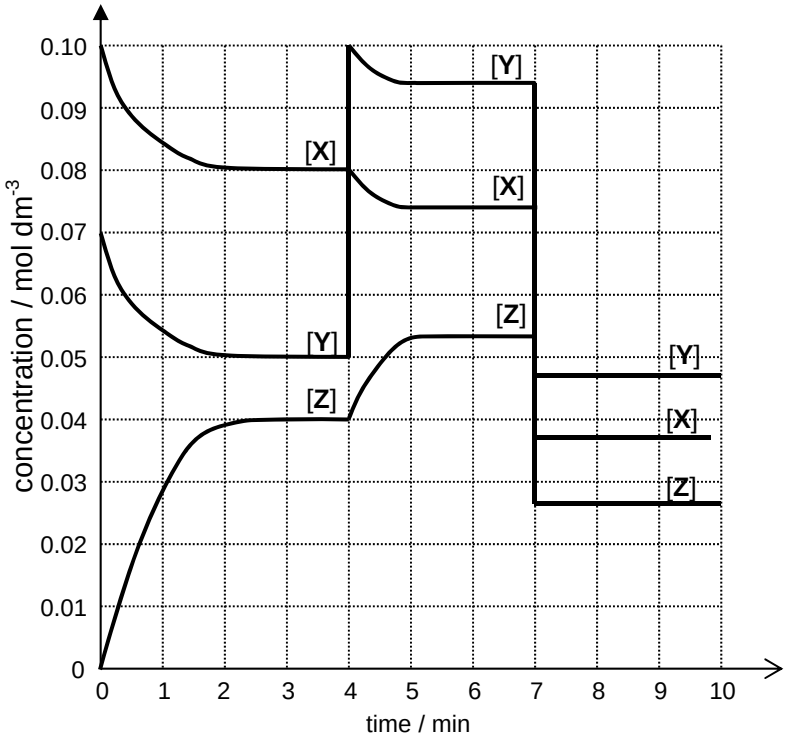
[8]

[Total: 20]

5. **(a)** **X** and **Y** were mixed in a closed vessel and the whole system was allowed to reach equilibrium, as shown in the following equation:

$$\mathbf{X}\,(g) + \mathbf{Y}\,(g) \rightleftharpoons 2\mathbf{Z}\,(g) \qquad \Delta H < 0$$

The concentrations of all gases were measured at one-minute intervals and the operating conditions were altered at the 4th and the 7th minute. The effects are shown in the graph below.



(i) Write an expression for the equilibrium constant, K_C, and hence calculate its value at the 3rd minute.

(ii) Suggest the change that could have occurred at the:

I 4th minute

II 7th minute

[4]

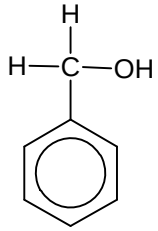
(b) A current of 300 A was passed through molten potassium bromide for 40 min at 450K and 1.21 x 10^5 Pa. A gaseous product was obtained at one of the electrodes.

(i) Write the equations of the reactions occurring at the anode and the cathode.

(ii) Determine the volume of the gas produced.

5. **(b)** **(iii)** The gas produced was reacted with propene. Outline the mechanism of the reaction.

(iv) The gas produced also reacts with phenylmethanol under different conditions to yield different products. Phenylmethanol has the following structure.



phenylmethanol

Draw the structure of the product when the reaction takes place under the following conditions:

I in the presence of sunlight

II in the presence of iron

[8]

(c) Compound **C**, C_5H_9OCl, does not react with thionyl chloride but forms an orange precipitate with 2,4-dinitrophenylhydrazine. When refluxed with hot aqueous potassium hydroxide, **C** forms **D**, $C_5H_{10}O_2$.

D does not form any yellow precipitate with alkaline iodine solution. When treated with acidified potassium dichromate(VI), **D** gives compound **E**.

In the presence of hot concentrated sulfuric acid, **E** forms a sweet-smelling liquid, **F**, $C_{10}H_{16}O_4$.

Suggest the structural formulae of compounds **C** to **F**, explaining the chemistry involved.

[8]

[Total: 20]

END OF PAPER